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54 **Phosphate-free detergent bleach compositions.**

57 Phosphate-free, aluminosilicate-built detergent bleach compositions having really effective cleaning and stain removal performances at low wash temperatures of 40°C and below are disclosed, which compositions comprise at least one detergent-active material, from 15% to about 40% by weight of a water-insoluble, aluminosilicate cation-exchange material, from 0.5 to about 3% by weight of a polyphosphonate compound, and from about 1% to about 5% by weight of a solid organic peroxyacid compound as the principal bleaching agent, said composition being substantially free of additional builder materials selected from the group consisting of citric acid and its alkali metal salts, bicarbonates, nitrilotriacetates and mixtures thereof. In a preferred embodiment the composition further contains an enzyme, particularly a proteolytic enzyme.

EP 0 313 145 A2

PHOSPHATE-FREE DETERGENT BLEACH COMPOSITIONS

This invention relates to phosphate-free detergent bleach compositions. In particular it relates to aluminosilicate built laundry detergent bleach compositions having improved cleaning and stain-removal performances.

The role and value of phosphate detergency builders in laundry detergent compositions are well-known. In recent years, however, the use of phosphate builders, such as the alkali metal triphosphates, has come under scrutiny because of the suspicion that soluble phosphate species accelerate the eutrophication of water bodies. In a number of countries phosphate legislations have already forced detergent manufacturers to radically reduce the phosphate level of detergent compositions down to substantially zero. The need exists, therefore, for a built laundry detergent composition with zero phosphate level but which is comparable to a conventional triphosphate built composition in overall detergency effectiveness.

Furthermore, with the present trend to lower fabric washing temperatures, there is an incentive to improve on the formulations of detergent compositions so as to be effective at lower washing temperatures of e.g. 40°C and below.

Water-insoluble aluminosilicates, commonly known as zeolites, have been used in detergent compositions as important alternative builders to phosphates (see, for example, GB-A-1429143; GB-A-1470250; GB-A-1504211; GB-A-1529454 and US-A- 4064062).

It is known that organic peroxyacids as a class are effective bleaching agents in the lower wash temperature region of, say, 40°C-60°C. Bleaching experiments have indicated that organic peroxyacids, e.g. 1,12-diperoxydodecanedioic acid, provide effective bleaching and stain removal at 40°C in a phosphate-built detergent formulation, but remarkably they are much less effective in non-phosphate, aluminosilicate-built detergent compositions.

It is an object of the present invention to provide an improved phosphate-free aluminosilicate built detergent composition having really effective cleaning and stain-removal performances at low wash temperatures of 40°C and below.

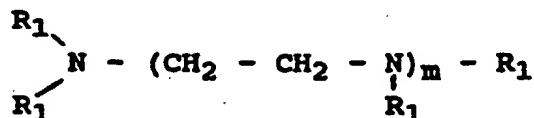
It has now been found that the above object can be achieved by using a solid organic peroxyacid compound as principal bleaching agent together with at least 0.5% by weight of a polyphosphonate sequestering agent.

Polyphosphonates have already been suggested for use in detergent compositions containing aluminosilicates. For example, German Offenlegungsschrift 2,544,035 ; 2,539,071 ; 2,527,388 ; 2,559,631 and Austrian patent N° 338,947 all disclose the use of various polyphosphonates notably as dispersing agents in aluminosilicate-built products.

EP-B1-0001853 discloses aluminosilicate-built detergent compositions containing 0.01-4% by weight of a polyphosphonate compound and 5-25% by weight of citric acid, citrates or a bicarbonate as pH-regulating agent such that the detergent composition has a solution-pH in the range from 7 to 9.5. The compositions as taught here in order to be effective still require a certain amount of a phosphate builder. They are furthermore unsatisfactory when used for washing at the low temperature region of 40°C and below.

Mixtures of certain polyphosphonates have also been suggested for use in detergent compositions containing a water-insoluble aluminosilicate builder according to EP-A-0168373. It is taught here that, from a functional point of view, it is advantageous to include additional builders, such as phosphates (5-20% by weight) and sodium nitrilotriacetate (2-10% by weight). Though some organic peroxyacids are mentioned, the peroxygen bleaching compound as meant and used here is a compound which is capable of yielding hydrogen peroxide in aqueous solution, e.g. sodium perborate. Organic peroxyacids do not belong to this category.

Thus, according to the invention there is provided a phosphate-free detergent bleach composition comprising at least one detergent-active material, from 15% to about 40% by weight of a water-insoluble aluminosilicate cation-exchange material, and from 0.5% to about 3% by weight of a polyphosphonate compound of the formula:



wherein each R_1 is $\text{CH}_2\text{PO}_3\text{H}_2$ or a water-soluble salt thereof, and m is an integer having the value of 0, 1 or 2, characterized in that the composition contains from about 1% to about 15% by weight of a solid organic peroxyacid compound as the principal bleaching agent, said composition being substantially free of additional builder materials selected from the group consisting of citric acid and alkali metal salts thereof, bicarbonates, nitrilotriacetates and mixtures thereof.

Preferably, the composition of the invention will also include an enzyme, particularly proteolytic enzymes. Suitable proteolytic enzymes are normally solid, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the composition of the present invention. Examples of suitable proteolytic enzymes are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*, such as the commercially available subtilisins Maxatase®, as supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase®, as supplied by Novo Industri A/S, Copenhagen, Denmark.

Particularly suitable is a protease obtained from a strain of *Bacillus* having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novo Industri A/S under the registered trade names Esperase® and Savinase®. The preparation of these and analogous enzymes is described in British Patent Specification No 1,243,784.

The amount of proteolytic enzymes used in the composition of the invention ranges from 0.001% to 10% by weight, preferably from 0.01% to 5% by weight, depending upon their activity. They are generally incorporated in the form of granules, pills or "marumes" in an amount such that the final washing product has a proteolytic activity of from about 2-20 Anson units per kilogram of final product.

The composition of the invention contains at least one detergent-active material which can be an organic soap or synthetic detergent surfactant material. Generally, from about 5% to 40% by weight of an organic, anionic, nonionic, amphoteric or zwitterionic detergent compound, soap, or mixtures thereof is included. Many suitable detergent-active compounds are commercially available and are fully described in literature, for example in US-A-4222905 and US-A-4239659 and in "Surface Active Agents and Detergents", Vol. I and II, by Schwartz, Perry and Berch.

The preferred detergent-active compounds which can be used are synthetic anionic, soap and nonionic compounds. The first-mentioned are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher aryl radicals. Examples of suitable synthetic, anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C_8 - C_{18}) alcohols produced, for example, from tallow or coconut oil; sodium and potassium alkyl (C_9 - C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10} - C_{15}) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those esters of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_9 - C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralized with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphates such as those derived by reacting alpha-olefins (C_8 - C_{20}) with sodium bisulphate and those derived by reacting paraffins with SO_2 and Cl_2 and then hydrolyzing with a base to produce a random sulphonate; olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10} - C_{20} alpha-olefins, with SO_3 and then neutralizing and hydrolyzing the reaction product. Suitable soaps are the alkali metal salts of long chain C_8 - C_{22} fatty acids such as the sodium soaps of tallow, coconut oil, palmkernel oil, palm oil or hardened rapeseed oil fatty acids or mixtures thereof. The preferred anionic detergent compounds are sodium (C_{11} - C_{15}) alkyl benzene sulphonates and sodium (C_{16} - C_{18}) alkyl sulphates.

Examples of suitable nonionic detergent compounds which may be used include the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6 - C_{22}) phenols, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule; the condensation products of aliphatic (C_8 - C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally 6 to 30 EO, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylene diamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulfoxides.

Mixtures of detergent-active compounds, for example mixed anionic or mixed anionic and nonionic compounds, may be used in the detergent compositions, particularly in the latter case to provide controlled low sudsing properties. This is beneficial for compositions intended for use in suds-intolerant automatic

washing machines.

Amounts of amphoteric or zwitterionic detergent-active compounds can also be used in the compositions of the invention, but this is not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic, detergent-active compounds are used, it is generally in small amounts in the compositions based on the much more commonly used synthetic anionic and/or nonionic detergent-active compounds.

The detergent composition of the invention also contains a water-insoluble aluminosilicate cation-exchange material in an amount of from 15% to about 40% by weight, preferably from 20% to 35% by weight.

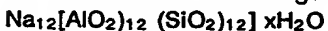
The aluminosilicate can be crystalline or amorphous in character, preferred materials having the unit cell formula I



wherein M is a calcium-exchange cation, z and y are at least 6; the molar ratio of z to y is from about 1.0 to about 0.5 and x is at least 5, preferably from about 7.5 to about 276, more preferably from about 10 to about 264. The aluminosilicate materials are in hydrated form and are preferably crystalline containing from about 10% to about 28%, more preferably from about 18% to about 22% water.

The aluminosilicate ion-exchange materials are further characterized by a particle size diameter of from about 0.1 micron to about 10 microns, preferably from about 0.2 micron to about 4 microns. The term "particle size diameter" herein represents the average particle size diameter of a given ion-exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope. The aluminosilicate ion-exchange materials herein are usually further characterized by their calcium ion-exchange capacity, which is at least about 200 mg. equivalent of $CaCO_3$ water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from about 300 mg eq./g to about 352 mg eq./g. The aluminosilicate ion-exchange materials herein are still further characterized by their calcium ion-exchange rate which is at least about 2 grains Ca^{++} /gallon/minute/gallon of aluminosilicate (anhydrous basis), and generally lies within the range of from about 2 grains/gallon/minute/gram/gallon to about 6 grains/gallon/gram/gallon, based on calcium ion hardness. Optimum aluminosilicates for builder purposes exhibit a calcium ion-exchange rate of at least about 4 grains/gallon/minute/gram/gallon.

Aluminosilicate ion-exchange materials useful in the practice of this invention are commercially available and can be naturally occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion-exchange materials is discussed in US-A-3985669. Preferred synthetic crystalline aluminosilicate ion-exchange materials useful herein are available under the designations Zeolite A, Zeolite B, Zeolite X, Zeolite HS and mixtures thereof. In an especially preferred embodiment, the crystalline aluminosilicate ion-exchange material is Zeolite A and has the formula



wherein x is from about 20 to about 30, especially about 27. Zeolite x of formula $Na_{86} [(AlO_2)_{86} (SiO_2)_{106}] \cdot 276 H_2O$ is also suitable, as well as Zeolite HS of formula $Na_6 [(AlO_2)_6 (SiO_2)_6] \cdot 7.5 H_2O$.

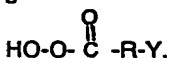
The polyphosphonate compounds usable in the present invention are as defined hereinbefore. Effectively, the amount of polyphosphonate compound in the composition is from 0.5% to about 3% by weight. Amounts of lower than 0.5% are inadequate to give the desired benefit and levels of higher than 3% by weight will give no added benefit. A preferred level of polyphosphonate compound is from 1% to 2% by weight of the composition.

Suitable polyphosphonate compounds are, for example, aminotri (methylene phosphonic acid), ethylene diamine tetra(methylene phosphonic acid) and diethylene triamine penta(methylene phosphonic acid).

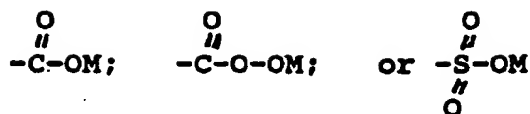
A preferred polyphosphonate compound is ethylene diamine tetra(methylene phosphonic acid) or its water-soluble salts, known as EDTMP, which is preferably used in the form of its calcium complex, i.e. Ca_n -EDTMP (n being from 1-3), as disclosed in US-A-4,259,200.

A further essential component of the compositions herein is from about 1% to about 15% by weight, preferably from 2% to 10% by weight of a solid organic peroxyacid compound. The organic peroxyacid compounds used in the present invention are solid at room temperature and should preferably have a melting point of at least 50 °C.

Such peroxyacid compounds are the organic peroxyacids and water-soluble salts thereof having the general formula:

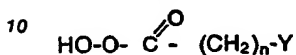


wherein R is an alkylene or substituted alkylene group containing 1 to 20 carbon atoms or an arylene group containing from 6 to 8 carbon atoms, and Y is hydrogen, halogen, alkyl, aryl or any group which provides an anionic moiety in aqueous solution. Such Y groups can include, for example :



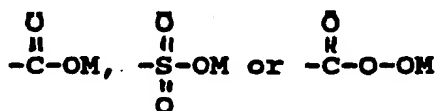
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wherein M is H or a water-soluble, salt-forming cation. The organic peroxyacids and salts thereof usable in the present invention can contain either one, two or more peroxy groups and can be either aliphatic or aromatic. When the organic peroxyacid is aliphatic, the unsubstituted acid may have the general formula:



wherein Y can be H, -CH₃, -CH₂Cl,

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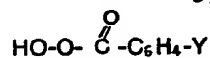


20 and n can be an integer from 6 to 20.

Peroxydodecanoic acids, peroxytetradecanoic acids and peroxyhexadecanoic acids are the most preferred compounds of this type, particularly 1,12-diperoxy-dodecanedioic acid, 1,14-diperoxy-tetradecanedioic acid and 1,16-diperoxyhexadecanedioic acid. Examples of other preferred compounds of this type are diperoxyazelaic acid, diperoxyadipic acid and diperoxysebacic acid.

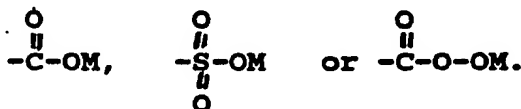
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When the organic peroxyacid is aromatic, the unsubstituted acid may have the general formula:



wherein Y is, for example, hydrogen, halogen, alkyl,

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35 The percarboxy and Y groupings can be in any relative position around the aromatic ring. The ring and/or Y group (if alkyl) can contain any non-interfering substituents such as halogen or sulphonate groups. Examples of suitable aromatic peroxyacids and salts thereof include monoperoxyphthalic acid, diperoxyterephthalic acid, 4-chlorodiperoxyphthalic acid, diperoxyisophthalic acid, m-chloroperoxybenzoic acid, p-nitroperoxybenzoic acid, and peroxy- α -naphthoic acid. A preferred aromatic peroxyacid is diperoxyisophthalic acid.

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A particularly preferred peroxyacid for use in the present invention is 1,12-diperoxydodecanedioic acid.

Apart from the components already mentioned, the detergent composition herein can contain any of the conventional additives and adjuncts in the amounts in which such materials are normally employed in fabric washing compositions. Examples of such additives include lather boosters such as alkanolamides, particularly the monoethanolamides derived from palmkernel and coconut fatty acids; lather depressants such as alkyl phosphates, silicones and waxes; anti-redeposition agents such as sodium carboxymethyl cellulose (SCMC), polyvinyl pyrrolidone (PVP) and the cellulose ethers such as methylcellulose and ethyl hydroxyethyl cellulose; stabilizers such as ethylene diaminetetraacetate; fabric softening agents; inorganic salts such as sodium sulphate and sodium carbonate; and - usually present in very minor amounts - fluor scent agents, perfumes, enzymes, particularly proteases, and other enzymes such as amylases and lipases; germicides and colourants.

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Polycarboxylate polymers, though not essential, may also be included as desired in amounts of e.g. from about 0.5% to 6% by weight of the total composition. The polycarboxylate polymers herein are preferably selected from co-polymeric polycarboxylic acids and their salts derived from an unsaturated polycarboxylic acid such as maleic acid, citraconic acid, itaconic acid or mesaconic acid as a first monomer and ethylene, methyl vinyl ether, acrylic acid or metacrylic acid as a second monomer, the co-polymer comprising at least about 10 mole%, preferably at least about 20 mole% of polycarboxylic acid units and having weight average molecular weights of at least about 10,000, preferably at least about 30,000;

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homopolyacrylates and homopolymethacrylates having a weight average molecular weight of from about 1000 to about 80,000, preferably from about 5000 to about 50,000; and mixtures thereof.

Additionally, the compositions may optionally and preferably include an inorganic peroxide compound, such as the alkali metal perborates, percarbonates, perphosphates and persulfates, the perborates, particularly sodium perborate tetra- and monohydrates, being preferred because of their commercial availability. If added, they may be present in an amount of from about 2 to 20% by weight of the final composition. These inorganic peroxide compounds will have the effect of improving high temperature performance.

The detergent compositions of the invention are preferably presented in free-flowing particulate, e.g. powdered or granular form, and can be produced by any of the known techniques commonly employed in the manufacture of such washing compositions, but preferably by spray-drying an aqueous slurry comprising the surfactant(s) and the alumino-silicate builder component to form a detergent base powder, to which the heat-sensitive ingredients are added, including the organic peroxyacid, peroxide compound, enzymes and optionally some other ingredients as conveniently desirable. The polyphosphonate compound may be present in the base powder, but is preferably added as calcium phosphonate to the spray-dried base powder. It is preferred that the process used to form the compositions should result in a product having a moisture content of up to about 15%, more preferably from about 7% to about 14% by weight.

The detergent compositions of the invention are generally alkaline and will advantageously have a pH (at 2-10 g/l) in aqueous solution of from about 8-11.

The invention will now be illustrated by the following non-limiting Examples.

Example I

The following particulate non-phosphate detergent composition was prepared by spray-drying an aqueous detergent slurry to form a detergent base powder composition (A) which is combined with a particulate product composition (B).

Composition A	Parts by weight
Sodium linear alkylbenzene sulphonate	9.0
Fatty alcohol-7 ethoxylate	1.5
Maleic acid/acrylic acid copolymer (Sokalan ® CP5 ex BASF)	4.0
Sodium aluminosilicate (Zeolite A)	24.0
Sodium sulphate (anhydrous)	0.3
Sodium carboxymethyl cellulose	0.5
Sodium ethylenediamine tetraacetate (EDTA)	0.2
Sodium carbonate (Na ₂ CO ₃)	2.0
Water and fluorescer (0.13)	7.6
Composition (B)	
Sodium perborate monohydrate	8.0
Anti-foaming agent	2.5
Proteolytic enzyme (Savinase ex NOVO)	0.5
Diperoxydodecanedioic acid (DPDA)	6.0
Sodium sulphate	33.9

Washing experiments were carried out with this composition without and with added tricalcium complex of EDTMP (Ca₃-EDTMP) at a level of 1% by weight in 30 minutes' Tergotometer washes using a dosage of 8 gram/litre in 24 ° FH water at 40 ° C, buffered at pH 8.5.

The bleaching properties on tea and red-wine stains, detergency and protein stain removal (enzyme action) were measured; the results are given in Table I.

Table I

		ΔR values			
		Tea	Wine	Detergency	Protein stains
Composition A/B		8.0	25	22.3	17.1
"	+ 1% $\text{Ca}_3\text{-EDTMP}$	18.7	39.2	25.7	33.0

The excellent overall cleaning and bleaching performance of the detergent composition of the invention at 40° C is clearly shown.

Example II

The experiments of Example I were repeated using the following base powder composition C and a combined composition A'/B.

Composition C	Parts by weight
Sodium dodecyl benzene sulphonate	9.0
Fatty alcohol-7-ethoxylate	4.0
Zeolite	24.0
Maleic acid/acrylic acid copolymer (Sokalan CP5 ex BASF)	4.0
Sodium carboxymethyl cellulose	0.5
EDTA	0.2
Sodium sulphate	44.1
Fluorescer	0.2
Water	8.0
Diperoxy dodecanediolic acid	6.0

Composition A' is Composition A without Sokalan CP5 copolymer.
The results are given in the following Table.

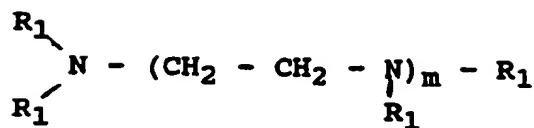
Table 2

		ΔR -values			
		Tea	Wine	Detergency	Protein stains
Composition C		6.9	21.6	21.5	27.6
"	+ 1% $\text{Ca}_3\text{-EDTMP}$	18.2	37.7	24.0	33.2
Composition A'/B		6.4	21.2	21.8	17.2
"	+ 1% $\text{Ca}_3\text{-EDTMP}$	18.6	37.9	23.1	32.4

The results show again the excellent overall cleaning and bleaching performances of the compositions according to the invention.

Claims

1. A phosphate-free detergent bleach composition comprising at least one detergent-active material, from 15% to about 40% by weight of a water-insoluble aluminosilicate cation-exchange material, and from 0.5% to about 3% by weight of a polyphosphonat compound of the formula:



wherein each R_1 is $CH_2PO_3H_2$ or a water-soluble salt thereof, and m is an integer having the value of 0, 1 or 2, characterized in that the composition contains from about 1% to about 15% by weight of a solid organic peroxyacid compound as the principal bleaching agent, said composition being substantially free of additional builder materials selected from the group consisting of citric acid and its alkali metal salts, bicarbonates, nitrilotriacetates and mixtures thereof.

2. A composition according to Claim 1, characterized in that it further comprises a proteolytic enzyme in an amount such that the final washing product has proteolytic activity from about 2 to 20 Anson units per kilogram of product.

3. A composition according to Claim 1 or 2, characterized in that said polyphosphonate compound is present in an amount of 1% to 2% by weight of the composition.

4. A composition according to Claim 1, 2 or 3, characterized in that said polyphosphonate compound is ethylene diamine tetra(methylene phosphonic acid) or its water-soluble salts.

5. A composition according to Claim 4, characterized in that said ethylene diamine tetra(methylene phosphonic acid) is present in the form of its calcium complex.

6. A composition according to any of the above Claims 1-5, characterized in that said organic peroxyacid is 1,12-diperoxydodecanedioic acid.

7. A composition according to any of the above Claims 1-6, characterized in that said aluminosilicate cation-exchange material is a zeolite selected from the group consisting of zeolite A, zeolite B, zeolite X and zeolite HS.

(19)



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(54) Phosphate-free detergent bleach compositions.

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(57) Phosphate-free, aluminosilicate-built detergent bleach compositions having really effective cleaning and stain removal performances at low wash temperatures of 40°C and below are disclosed, which compositions comprise at least one detergent-active material, from 15% to about 40% by weight of a water-insoluble, aluminosilicate cation-exchange material, from 0.5 to about 3% by weight of a polyphosphonate compound, and from about 1% to about 5% by weight of a solid organic peroxyacid compound as the principal bleaching agent, said composition being substantially free of additional builder materials selected from the group consisting of citric acid and its alkali metal salts, bicarbonates,

nitrilotriacetates and mixtures thereof. In a preferred embodiment the composition further contains an enzyme, particularly a proteolytic enzyme.



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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D, Y	EP-A-0 168 373 (MONSANTO) * Page 4, lines 30-37; page 7; claims 1-3, 6 *	1-7	C 11 D 3/395 C 11 D 3/12 C 11 D 3/36
Y	EP-A-0 137 669 (PROCTER & GAMBLE) * Claims 1, 11; page 19, lines 13-19, 34-35; page 23, line 3 *	1-7	
A	FR-A-2 388 043 (LAPORTE INDUSTRIES) * Page 11, lines 21-28; page 14, lines 3-4; page 13, lines 20-21; claims 1, 10, 11 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 11 D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20-07-1989	Examiner PFANNENSTEIN H. F.
CATEGORY OF CITED DOCUMENTS			
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